

A STUDY OF SYNTHESIS AND CHARACTERISATION OF Bi_2Te_3 -PANI WITH AND WITHOUT SELENIUM DOPING

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Abstract. *In this paper, our main objective is to have a methodical study of production and thermoelectric property of Bi_2Te_3 -PANI with and without Selenium doping. A comparison has drawn between the thermoelectric properties of Bi_2Te_3 -PANI with that of the pure Polyaniline (PANI). Pure PANI as well as Bi_2Te_3 -PANI composite was synthesized with the help of chemical oxidative technique. The thermal and electrical characteristics have been studied for both doped and undoped Bi_2Te_3 -PANI and it has been seen the thermal conductivity has been decreased for the doped sample. On the other hand, the electrical conductivity and conduction power is high in the case of doped Bi_2Te_3 -PANI in comparison to pure PANI. All these results leads us to the conclusion that Selenium doped Bi_2Te_3 -PANI has the characteristics of perfect thermoelectric material.*

Key works: Bi_2Te_3 -PANI, Conductivity, Doping, Figure of merit, Thermoelectric property.

1. INTRODUCTION

One of the most feasible substitute energy sources for today's world is thermoelectric energy. This no pollution energy source is able to trim down our reliance on carbon based fossil fuels and nuclear energy [1, 2]. All the alternative heat energy sources like solar, geothermal etc. can be transformed into electricity by using thermoelectric energy devices which are easy to construct and handle. Thermoelectric materials have been used in thermoelectric (TE) devices which obtain electricity from ravage heat emitted from industry and vehicles[3, 4]. Only 30-40% heat energy has been used to generate of electricity and rest of energy input is lost as ravage heat. Thermoelectric materials can transform ravage heat into electricity. This conversion efficiency from heat into electricity is related to intrinsic electrical and thermal properties. Electrical conductivity is a measure of how well

electrical current can pass through a material under the influence of an applied voltage/electric field. Thermal conductivity measures how well heat can pass through a material under a temperature differential.

The efficiency of thermoelectric materials is related to a dimensionless quantity, the thermoelectric figure of merit ZT, which can be defined as

$$ZT = (\sigma S^2) T / \kappa = PT / \kappa \quad (1)$$

Where σ represents the electrical conductivity, S represents the Seebeck coefficient, κ represents the thermal conductivity, and T represents the absolute temperature. The product σS^2 has been called as the TE power factor P[4, 5]. Therefore, by increasing S while keeping the optimum, the values that increase the power factor (σS^2) are prime which can be termed as the important approach for obtaining high efficiency thermoelectric material.

At present, all of the hard works are done on modifying the TE properties by different methods, like doping [6], nanostructuring, nanocomposite formation, and molecular rattling, and hence Polymer composites becomes an important part in this industry[7]. The properties shown by conducting polymers at very little temperature has many uses namely minimum price of manufacture, low weight, and flexibility[8].

Several scientists have studied Polyaniline (PANI) [9]. PANI is particularly important as it is fairly low-cost and has three separate oxidation states with special colors and also it responds to acid/base doping. TE can transform heat energy straight into electricity which can be used if necessary. It proposes a capable knowledge to transform heat energy from solar energy. It has also been used to recover ravage heat from manufacturing areas and vehicle exhausts. The TE efficiency of conducting polymer depends on the material[10, 11].

The power factor of TE should be made the most of and the thermal conductivity should be reduced to attain TE materials which have high energy adaptation efficiency[12]. Telluride induced materials usually show high thermoelectric power. As per earlier studies telluride based materials exhibits a TE figure of merit “ZT” upto 2.2, the maximum value claimed. For real life use, such as thermo-electric generators (TEGs) has the value of ZT is up to 3[13, 14].

A number of authors have worked on synthesise and character analysis of Bi_2Te_3 with polyaniline[4]. Mechanical unification technique was used newly by [15] for the production of Bi_2Te_3 -PANI. It was established that the power factor of Bi_2Te_3 -PANI is lesser than the two individual components. Again, a research work has been published on the production of Bi_2Te_3 -PANI mixture by physical addition and mixture displayed a greater power factor[15]. A number of publications are available on TE characteristics of Bi_2Te_3 -PANI, experimental research on TE property related to complexes are unobtainable. With all these literature review, in the current work, we have done a methodical understanding of synthesis and properties of Bi_2Te_3 -PANI. We also have studied the thermo-electric characteristic of Bi_2Te_3 -PANI after doping using Selenium.

EXPERIMENTAL METHODOLOGY-

Pure polyaniline polymer (PANI) synthesis - Pure polyaniline polymer water was synthesized by chemical oxidation method [16]. Aniline is oxidized with ammonium persulfate in acidic water. Dissolve separately in HCl and double distilled water. Both the liquids were mixed together at room temperature. Then the mixture was stirred for 1 h and allowed to polymerize. The PANI precipitate was collected using filter paper and washed with distilled water HCl and methanol, respectively. PANI powder was dried in vacuum [17].

The Bi_2Te_3 are purchased in the powder form from Sigma company with 99.99% purity.

Synthesis of Bi_2Te_3 -PANI - A dilute aniline solution is obtained to prepare these nanocomposites. Bismuth telluride was mixed with the liquid and stirred for 30

min[18]. The color associated with the solution has been changed to black. Now add APS as oxidizing agent and stir the entire mixture at 0-5 °C for 6 h for polymerization. The final mixture is a black-green colored PANI Bi_2Te_3 nanocomposite precipitate formed after vacuum drying in a 5 °C oven for an entire day [19].

DOPING USING Se

Se powder was used to dope Bi_2Te_3 -PANI and mix the ingredients in a container. Evenly, using deionized water as solvent, NaOH as pH regulator, NaBH_4 It is a reducing agent, EDTA is a coating agent, and it is transferred to In the WDF type high pressure reactor, keep it at 200°C for 8hr, then cool to room temperature, mixed solution was suction filtered and used repeatedly wash with deionized water and absolute ethanol, and finally vacuum dry at 60°C After 6 h, Se doped Bi_2Te_3 -PANI residue was obtained.

CHARACTERIZATION-

X-ray diffraction (XRD) as well as Fourier transform infrared (FTIR) characterization was used for Bi_2Te_3 -PANI and pure PANI. The structures of the sample were analyzed by XRD and FTIR in MNIT, Jaipur. The electrical properties like electrical conductivity were carried out through four probe method in MNIT,Jaipur.

RESULTS AND DISCUSSIONS-

To have the enhanced electric conductivity, we can dope the sample using a adequate quantity of appropriate dopants. The Seebeck coefficient would be increased as we increase the use of dopant to the sample. The reason behind this is the Fermi energy gets enforced profoundly in conduction range with the increase number of charged carriers. Now Selenium (Se) has been considered as the doping agent. First we will consider Bi_2Te_3 -PANI composite without any Se doping and after analyzing the different characteristics, we will repeat the work for doped Bi_2Te_3 -PANI.

WITHOUT Se DOPING-

Figure no. 1 illustrated XRD patterns for pure PANI, and Bi_2Te_3 -PANI. All peak units associated with pure

PANI models are clearly marked. Compared to pure builder, the XRD contour of Bi_2Te_3 -PANI combination clearly shows a high peak at the same location. The observation of individual peaks is related to the periodic separation of repeating

polyaniline units and the molecular organization of Bi_2Te_3 in the PANI matrix. This indicates that Bi_2Te_3 -PANI results in a well-arranged molecular organization of Bi_2Te_3 in triplet combinations.

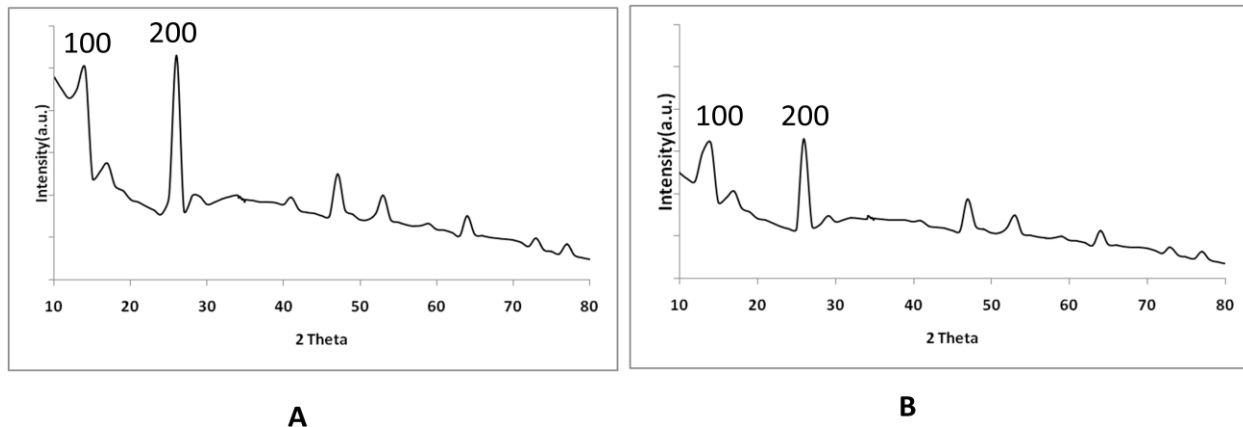


Fig. no. 1- (A) XRD pattern of Bi_2Te_3 -PANI (B) XRD pattern of pure PANI.

The Fourier transform of the above mentioned nanocomposite indicated the existence of a doped builder in the nanocomposite infrared spectra. One can see from Fig. no. 2, the peak transmittance at 798 cm^{-1} coincides with the semi-distributed benzene ring which is considered in the literature to be "electronic exploitation". The peaks at 1570.95 cm^{-1} correspond to the extended N-H bond of the benzoid ring (the upper characteristic of the cap) representing that the polymerization reaction was successfully completed and transformed into a PANI. The peak at 1114 represents the "electron like absorption". All the

discussion is for pure PANI. The peaks take place almost at the same position in case of Bi_2Te_3 -PANI. Electrometry involved taking measurements of the electrical conductivity related to nanocomposites using temperature. PANI is known to be an insulator as emeraldine base (EB) base. Doping turns PANI from insulator to conductor. PANI conductivity is largely reliant on the doping character. In this paper we doped PANI with Bi_2Te_3 and polymer to increase electrical conductivity. Although the carrier density increases with increasing temperature, the conductivity of PANI-nanocomposites remains low because of the low conductivity of Polyaniline.

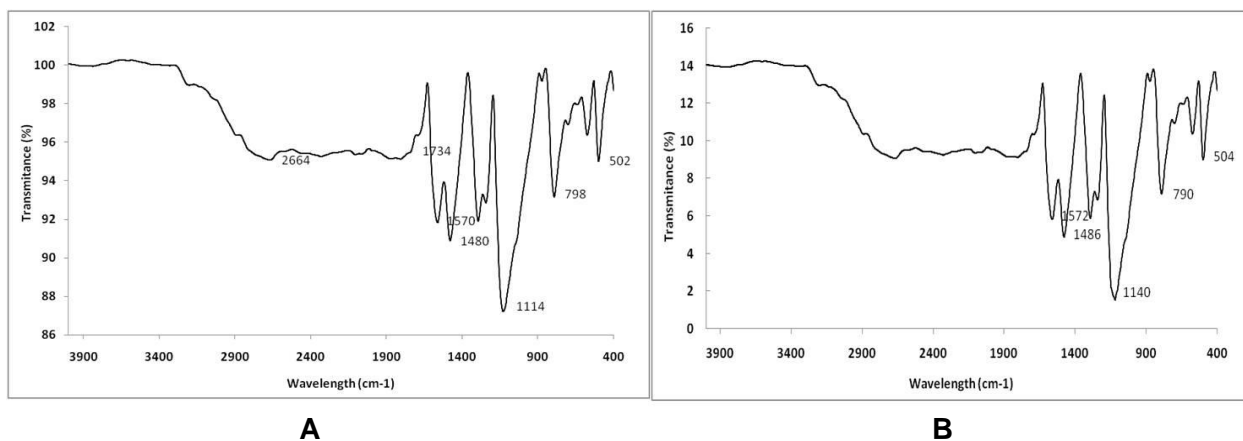


Fig. no. 2 - (A) FTIR spectra of pure PANI nanocomposite (B) FTIR spectra of Bi_2Te_3 -PANI nanocomposite.

This is because nanofilter energy barrier was created in the polymer chain, now the charge carriers should overcome this barrier. But a slight initial increase in the PANI's conductivity can be observed as it contains Bi_2Te_3 inorganic compound.

Both the PANI and the Bi_2Te_3 increases the conductivity of electricity with temperature. The electrical conductivity of Bi_2Te_3 -PANI over the entire temperature range is more in comparison to pure cells. This might be because of the generation of the molecular organization of Bi_2Te_3 in Bi_2Te_3 -PANI complex formulation due to the large surface area that PANI provides to Bi_2Te_3 .

WITH Se DOPING-

The connection between conduction rate and temperature can be observed from the figure. Bi_2Te_3 -PANI sample's conductivity decreases with increasing temperature. As we increase the doping of Se, the conductivity fluctuates dramatically. The thermal conductivity gradually decreases to the lowest value. Significant loss in thermal conductivity is due to doping. The alloy scattering not only reduces the carrier mobility related to the sample, but also it increases the scattering effect on phonons, which considerably reduces the lattice thermal conductivity related to the product. In this stage, the thermal conductivity of the material comes largely from the input of the low-frequency photons. The grain boundary effect dispersion increased relatively and became large, which reduced the mean free path and thermal conductivity related to the photons.

Table no. 1- Comparison of the Room Temperature Transport Parameters (σ , S, κ , P, and ZT) between Bi_2Te_3 -PANI with and without Se doping under room temperature.

Composite	σ (S cm^{-1})	S(μ V m^{-1} K $^{-1}$)	P(μ W m^{-1} K $^{-2}$)	κ (W m^{-1} K $^{-1}$)	ZT
Bi_2Te_3 -PANI without Se doping.	11.62	36.8	1.57	0.11	0.0042
Bi_2Te_3 -PANI with Se doping	25.01	102.22	26.13	0.19	0.041

The thermal conductivity related to the substrate decreases with the enlargement of the amount of Se doping. On the one hand, the doping of Se would increase the carrier concentration, which leads to an

increase in electrical conductivity. The above mentioned discussion helps in finding an inference that Se doping has a significant influence on Bi_2Te_3 -PANI's morphology in a positive direction regarding the electrical conductivity.

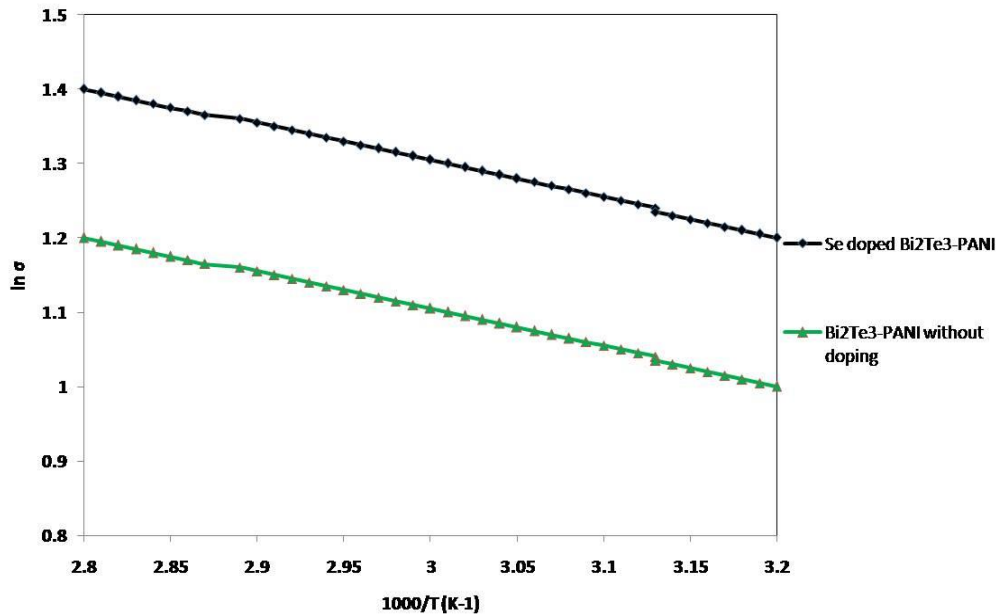


Fig. no. 3- The electrical measurements of Bi₂Te₃-PANI composite with and without Se doping.

From the Table no. 1 we can see the value of ZT increases with Se doping and we already have mentioned the efficiency of TE materials depends on ZT, we can clearly say that, Se doping has made Bi₂Te₃-PANI a better thermoelectric material.

Fig3 shows how the conductivity changes with respect to temperature. The conductivity increases with the doping.

CONCLUSIONS

The Bi₂Te₃-PANI was successfully synthesized and doped with Selenium. Increase in the three order magnitudes of conductivity have been observed after doping. Conduction mechanism has been explained. From thermal studies it is obvious that the conductivity increases with the rise in Se concentration followed by decline. The released enthalpy has been found to be associated with polymer metastability. It is quite clear from the studies that there are some structural changes of PANI after doping of Se due to which it becomes a better TE material, though it is quite clear from literature survey that conductivity depends on the

amount of doping. Extreme amount of doping could lead to lesser conductivity.

As the amount of Se doping increases, the conductivity of the product after a certain large amount, decreases; the doping of Se element effectively decreases the thermal conductivity of the Bi₂Te₃-PANI than that of the undoped sample. Clearly a perfect amount of doping could lead to good quality of thermoelectric material.

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